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(71) Applicants
Mitsubishi Rayon Co.,
Ltd., 3—19, Kyobashi 2-
chome, Chuo-ku, Tokyo
104, Japan

(72) Inventors
Kazu Kishida,
Akira Hasegawa,
Masahiro Sugimori

(74) Agents
R. G. C. Jenkins & Co.,
Chancery House, 53/54
Chancery Lane, London
WC2A 1QU

(54) Delustered thermoplastic resin compositions

(57) A delustered thermoplastic resin compositions are obtained by incorporating in 100 parts of a thermoplastic resin up to 40 parts by weight of a cross-linked polymer having an average particle diameter of 35—500 μ which polymer is obtained by suspension-polymerizing a non-

cross-linking monomer composition comprising 0—90% of a vinyl aromatic monomer, 10—100% of an alkyl (meth)acrylate having 1—13 carbon atoms in the alkyl group and 0—40% of another monoethylenically unsaturated monomer with 0.5—5 parts per 100 parts of the non-cross-linking monomer composition, of a cross-linking monomer having at least two double bonds in the molecule.

SPECIFICATION

Delustered thermoplastic resin composition

The present invention relates to a delustered thermoplastic resin composition.

Molded articles of thermoplastic resins such as vinyl chloride resin, ABS resin and acrylic resin are generally lustrous. The lusters are important properties sometimes according to the use. On the other hand, such lusters are unnecessary in other cases or, for some purposes, the lusters are unpreferred.

Conventional processes for delustering thermoplastic resins may be divided roughly into the following processes:

- (1) Process wherein an inorganic or organic delustering agent is incorporated therein, and
- (2) Process wherein an after treatment such as delustering treatment is effected.

Process (2) is unsuitable in many cases when the fabrication is to be effected subsequently because of its poor productivity, high processing costs and insufficient delustering effect obtained, though deterioration in physical properties is small. Process (1) has a serious problem of a reduction in physical properties, though the productivity is substantially not reduced and delustering degree can be controlled according to this process and this process can be employed when the fabrication is to be effected subsequently. Particularly when an inorganic substance such as silica gel or calcium silicate is used as the delustering agent, physical properties such as impact resistance and load elongation are remarkably deteriorated and in many cases, the product thus obtained can not be used practically. On the other hand, as processes wherein an organic delustering agent, particularly, high molecular delustering agent, is used, there have been known (a) a process wherein liquid polybutadiene is used and (b) a process wherein an endopolymerization product of a mixture of cross-linked styrene/alkyl acrylate copolymer having an average particle diameter of 1—30 μ and a non-crosslinked resin is used. The former process invites a reduction in heat distortion temperature unfavorably. As for the latter process, in fact, it is quite difficult to obtain particles of the above average diameter of 1—30 μ by the ordinary emulsion polymerization or suspension polymerization. Further, the particles of such a size are too small to exhibit a sufficient delustering effect in the delustering treatment of ABS resin and polyvinyl chloride (PVC). In addition, the non-cross-linked resin introduced therein by the complicated endopolymerization technique reduces the delustering effect on the ABS and PVC to make the effects of the delustering agent insufficient, though the non-cross-linked resin increases compatibility thereof with ABS and PVC. Generally, in the delustering agents of a type to be incorporated in a substance to be delustered, it has been said that the delustering effect thereof runs counter to compatibility thereof with the thermoplastic resin. This fact has heretofore inhibited the development of a delustering agent having both the delustering effect and physical properties-maintaining effect.

The object of the present invention is to provide a novel delustering agent which causes only very slight deterioration in physical properties and which can be produced on an industrial scale.

Another object of the present invention is to provide a polymer having both delustering effect and compatibility by a very easy means such as suspension polymerization.

The present invention relates to a delustered thermoplastic resin composition obtained by incorporating in a thermoplastic resin a cross-linked polymer having an average particle diameter of 35—500 μ which polymer is obtained by suspension-polymerizing a non-cross-linking monomer composition comprising 0—90 wt.% of a vinyl aromatic monomer, 10—100 wt.% of an alkyl (meth)acrylate having 1—13 carbon atoms in the alkyl group and 0—40 wt.% of another monoethylenically unsaturated monomer with 0.5—5 parts by weight, per 100 parts by weight of the non-cross-linking monomer composition, of a cross-linking monomer having at least two double bonds in the molecule.

One of the characteristic features of the present invention resides in the diameter of the resulting polymer particles. Namely, the greatest effects are exhibited with particles of an average diameter of 35—500 μ , particularly 40—200 μ . If the average particle size is less than 35 μ , the delustering effects are insufficient. On the other hand, if the average particle size is more than 500 μ , the resultant molded articles have rough surfaces and it becomes difficult to effect the uniform delustering effect.

As to the monomers to be copolymerized for obtaining the cross-linked polymer, there is a suitable range of proportion thereof as well be described below. If the monomers are used in amounts outside said range, the physical properties are seriously damaged, though some delustering effect is obtained or, alternatively, the delustering effect obtained is only insufficient. Either way, it is surprising that polymers having both delustering effect and compatibility with thermoplastic resins can be obtained by a quite simple method such as the conventional suspension polymerization. Though the mechanism thereof has not been completely elucidated yet, it is considered that this fact is due to the composition distribution and cross-linking distribution in the resulting polymer particles.

Now, the description will be made on the monomer compositions suitable for obtaining the cross-linked polymers used as the delustering agents in the present invention.

The monomers used for the production of the cross-linked polymers in the present invention may be divided roughly into non-cross-linking monomers and cross-linking monomers.

As the non-cross-linking monomers, there may be mentioned vinyl aromatic monomers,

(meth)acrylic acid esters and, if necessary, other monoethylenically unsaturated monomers. They are used in amounts of 0—90 wt.% of the vinyl aromatic monomer, 10—100 wt.% of the alkyl (meth)acrylate having 1—13 carbon atoms in the alkyl group and less than 40 wt.% of the other monoethylenically unsaturated monomer.

5 The vinyl aromatic monomers include styrene, vinyltoluene, α -methylstyrene and halogenated styrenes. 5

The (meth)acrylic acid esters include preferably lower (meth)acrylic acid esters such as ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate.

10 The other monoethylenically unsaturated monomers include methacrylic acid, fumaric acid, maleic acid and copolymerizable carboxylic acids and their esters excluding the alkyl (meth)acrylates having 1—13 carbon atoms in the alkyl group, vinyl halides such as vinyl chloride and vinyl bromide, vinyl esters such as vinyl acetate and acrylonitrile. 10

15 As the cross-linking monomers, there may be used compounds having at least 2 unsaturated bonds in the molecule. Among them, compounds wherein at least one of the two or more unsaturated bonds is allyl group are preferred. By the use of such allyl group-containing cross-linking monomers, it becomes possible to realize a suitable cross-linking composition distribution in the cross-linked polymers. As typically allyl group-containing cross-linking monomers, there may be mentioned allyl methacrylate, triallyl cyanurate and triallyl isocyanurate. 15

20 As other cross-linking monomers, there may be mentioned unsaturated carboxylic acid esters of alkylene glycols such as ethylene glycol dimethacrylate, unsaturated alcohol ethers of alkylene glycols such as propylene glycol diallyl ether and polyvinylbenzenes such as divinylbenzene. 20

The cross-linking monomers are used in an amount of 0.5—5 parts by weight, particularly 1.5—4 parts by weight, per 100 parts by weight of the non-cross-linking monomers.

25 As initiators used in the suspension polymerization, there may be mentioned those generally used in the suspension polymerization in the prior art. As typical initiators, there may be mentioned organic peroxides such as benzoyl peroxide and lauroyl peroxide and azo compounds such as azobisisobutyronitrile. 25

30 As suspension stabilizers, there may be mentioned those generally used in the prior art. As typical suspension stabilizers, there may be mentioned organic colloidal high molecular substances such as polyvinyl alcohol, polyacrylic acid salts, carboxymethyl cellulose, gelatin and tragacanth, and inorganic colloidal substances such as barium sulfate, magnesium carbonate and calcium phosphate as well as combinations of them with surfactants. 30

35 The suspension polymerization is carried out generally by suspending the monomers in water together with a polymerization initiator in the presence of a suspension stabilizer. In another manner of the polymerization, a polymer soluble in the monomer may be dissolved therein prior to the polymerization. In still another manner of the polymerization, the bulk polymerization is carried out partially in the absence of the cross-linking monomer and then the suspension polymerization is carried out in the presence of the cross-linking monomer and the suspension stabilizer. 35

40 As a matter of course, a polymerization regulator such as n-octylmercaptan or t-dodecylmercaptan can be used in the polymerization. It is rather preferred in many cases to control the molecular weight distribution with the regulator. 40

45 As typical thermoplastic resins which can be delustered by incorporating the delustering agent (cross-linked polymer) used in the present invention, there may be mentioned vinyl chloride resin, ABS resin, acrylic resin, methacrylic resin, methyl methacrylate/butadiene/styrene resin (MBS resin), nylon, polyethylene, polyethylene terephthalate, polycarbonate, polyurethane, polystyrene and polypropylene. 45

The delustering agent is incorporated in the thermoplastic resin in an amount of preferably less than 40 parts by weight. The effects thereof can be exhibited sufficiently even in an amount of as small as less than 10 parts by weight.

50 If necessary, general additives such as a stabilizer, lubricant, processing acid, high impact resistance aid, plasticizer, foaming agent, filler and coloring agent may be incorporated in the composition of the present invention. 50

In the following examples, parts are given by weight.

EXAMPLE 1

55 (1) Preparation of cross-linked polymer (A): 55

The following compounds are charged in a reaction vessel provided with a stirrer, reflux condenser and nitrogen gas inlet:

Styrene	70 parts
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Ethyl acrylate	30
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60 Allyl methacrylate	2.5	60
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n-Octylmercaptan	0.1
Lauryl peroxide	0.5
Polyvinyl alcohol	0.5 part
Water	200 parts

- 5 After sufficiently replacing the gas in the reaction vessel with nitrogen gas, the mixture of the above compounds was heated to 75°C under stirring to carry out the polymerization in nitrogen gas stream. After 3 hours, the temperature was elevated to 85°C and the mixture was kept at that temperature for three hours and then the temperature was elevated to 95°C and the mixture was kept at that temperature for one hour to complete the polymerization. After dehydration followed by drying, cross-linked polymer (A) was obtained in the form of beads. 5 10

Particle size distribution of the resulting beads was as shown below:

Mesh	wt. %	
Lower than 24	1.2	
24 — 32	33.2	
32 — 48	33.5	15
48 — 100	30.1	
100 — 150	1.5	
150 — 200	0.4	
200 —	0.1	

- 20 The particle size distribution (numeral %) determined from a photomicrograph was as shown below. Average particle diameter was 142 μ . 20

Larger than 500 μ	1.8%	
300 — 500 μ	6.7%	
150 — 300 μ	36.0%	
100 — 150 μ	14.8%	25
75 — 100 μ	9.5%	
50 — 75 μ	20.3%	
25 — 50 μ	9.7%	
Smaller than 25 μ	1.2%	

- 30 (2) Preparation of delustered thermoplastic resin composition (example of the incorporation of the delustering agent into rigid PVC): 30

100 Parts of polyvinyl chloride ($\bar{P}=720$) were mixed with 3 parts of a stabilizer (dibutyltin maleate), 10 parts of a high impact resistance aid (METABLEN® C—102; a product of Mitsubishi Rayon Co.), 1.0 part of a processing aid (METABLEN® P—551; a product of Mitsubishi Rayon Co.), 1 part of a lubricant (n-butyl stearate) and 5 parts of cross-linked polymer (A) obtained in above process (1). The whole was kneaded by means of rolls at 165°C and 60° specular gloss of the product was measured. Then, the mixture kneaded with the rolls shaped into a plate of a thickness of 2.5 mm at 165°C under a pressure of 70 tons and V-notch Izod impact strength thereof was measured to obtain the results shown in Table 1. 35

- 40 For comparison, the measurement results of the four kinds of the composition having the same resin composition except that the cross-linked polymer (A) is not contained, 5 parts of silica gel, is contained in place of the cross-linked polymer (A), 5 parts of a commercial delustering agent is contained in place of the cross-linked polymer (A) or 5 parts of only fractions of the cross-linked polymer 40

(A) which passed a 500 mesh sieve ($25\ \mu$) is contained in place of the cross-linked polymer (A) as obtained are also shown in Table 1.

TABLE 1

	Izod impact value (Kg.cm/cm)	60°C Gloss (%)
Example 1	16.5	26
Comparative Example (1) (free of delustering agent)	20.7	83
Comparative Example (2) (containing silica gel)	0.7	48
Comparative Example (3) (containing a commercial delustering agent)	11.0	41
Comparative Example (4) (containing fractions of the cross-linked polymer (A) which passed a 500 mesh sieve; average particle diameter $14\ \mu$)	15.9	52

It is apparent from Table 1 that cross-linked polymer (A) used in the present invention exhibits a superior delustering property and imparts a superior impact resistance as compared with those of silica gel and the commercial delustering agent. If the average particle diameter of the cross-linked polymer is less than $35\ \mu$ as in Comparative Example (4), the delustering effect thereof is very poor.

EXAMPLE 2

(Example of the incorporation of the delustering agent into plasticised PVC):

100 Parts of polyvinyl chloride ($\bar{P}=1100$) were mixed with 50 parts of a plasticizer (dioctyl phthalate), 2.5 parts of a Cadmium stearate-Barium stabilizer, 0.3 part of stearic acid and 5 parts of cross-linked polymer (A) obtained in above Example 1-(1). The whole was kneaded by means of rolls at 155°C . 60° Specular gloss of the product was measured in the same manner as in Example 1 to obtain the results shown in Table 2.

For comparison, the measurement results of the same resin composition but free of the cross-linked polymer (A) and the same resins compositions but containing each 5 parts of silica gel or a commercial delustering agent in place of the cross-linked polymer (A) are also shown in Table 2.

TABLE 2

	60° Gloss
Example 2	32
Comparative Example (1) (free of delustering agent)	81
Comparative Example (2) (containing silica gel)	50
Comparative Example (3) (containing a commercial delust ring agent)	43

It is apparent from Table 2 that the cross-linked polymer (A) used in the present invention exhibits a superior delustering effect also on the plasticised PVC to those of silica gel and the commercial delustering agent.

EXAMPLE 3

(Example of the incorporation of the delustering agent into ABS resin):

100 Parts of ABS resin (DIAPET® 3001; a product of Mitsubishi Rayon Co.) were mixed thoroughly with 5 parts of cross-linked polymer (A) obtained in Example 1 by means of a Henschel mixer. The mixer was extruded by means of an extruder having a screw of a diameter of 40 mm at 230°C and cut into pellets. 5

Thus obtained pellets were dried and injection-molded into a plate of a thickness of 3 mm at 200°C. V-notch Izod impact strength and 60° Specular gloss of the plate were measured.

The results of the measurement are shown in Table 3, wherein the results obtained by using no delustering agent or using only fractions of cross-linked polymer (A) which passed a 500 mesh sieve (25 μ) are also shown. 10

TABLE 3

	Izod impact strength (kg.cm/cm ²)	60° Gloss
Example 3	23.7	32
Comparative Example (1) (free of delustering agent)	25.3	93
Comparative Example (2) (containing fractions of cross-linked polymer (A) which passed through a 500 mesh sieve; average particle diameter 14 μ)	24.0	78

It is apparent from Table 3 that the cross-linked polymer used in the present invention exhibits an excellent delustering effect also on the ABS resin and it does not significantly reduce the impact strength. As shown in Comparative Example (2), the cross-linked polymer having an average particle diameter of less than 35 μ exhibits a very poor delustering effect. 15

EXAMPLE 4

Cross-linked polymers were obtained by the polymerization reaction in the same manner as in Example 1-(1) except that non-cross-linking monomer compositions as shown in Table 4 were used and 0.2 part of t-dodecylmercaptan was used in place of 0.1 part of n-octylmercaptan. The resulting particles had an average particle diameter of around 150 μ according to microphotographs in all cases which were substantially equal to that of the cross-linked polymer obtained in Example 1-(1). 20

Compositions were prepared in the same manner as in Example 1-(2) except that the respective cross-linked polymers thus obtained were used. The compositions were kneaded with rigid PVC by means of rolls and compression-molded and glosses and Izod impact strengths of the molded articles were determined. The surface conditions (roughness, uniformity, etc.) were evaluated visually as the standards of the evaluation of dispersibilities. 25

The results are shown in Table 4 together with the results of comparative examples (wherein the compositions are beyond the range of the invention).

TABLE 4

	Non-cross-linking monomer composition						Physical properties of the composition		
	Styrene	Ethyl acrylate	n-Butyl acrylate	2-Ethyl-hexyl acrylate	Methyl-meth-acrylate	Acrylo-nitrile	60° Gloss	Izod impact strength (kg.cm/cm ²)	Surface Condition
Experiment (1)	90			10			22	14.2	β
" (2)	70	20	10				28	17.1	α
" (3)	60		20		20		26	17.5	α
" (4)	50	20	10		20		25	14.9	β
" (5)	50	30			10	10	24	14.7	β
" (6)			20		80		29	16.2	β
Comp. Ex. (1)	100						19	8.7	γ
" (2)	40					60	14	5.2	γ

α — very good: β — good: γ — poor

EXAMPLE 5

70 Parts of styrene, 30 parts of ethyl acrylate, 0.5 part of benzoyl peroxide, 1.0 part of calcium tertiary phosphate, 0.01 part of a surfactant, 200 parts of water and a cross-linking monomer in an amount shown in Table 5 were charged in the same reaction vessel as in Example 1-(1) to obtain a cross-linked polymer in the same manner as in Example 1-(1). The resulting cross-linked polymers had an average particle diameter of around 100 μ .

Compositions were prepared in the same manner as in Example 1-(2) except that the respective cross-linked polymers thus obtained were used. Physical properties of them were evaluated in the same manner as in Example 1-(2) and Example 4 to obtain the results shown in Table 5.

TABLE 5

	Cross-linking monomer				Physical properties of the composition		
	Allyl methacrylate	Triallyl cyanurate	BDMA	Divinylbenzene	60° Gloss	Izod impact strength (kg.cm/cm ²)	Surface condition
Experiment (1)	1				39	18.9	α
" (2)	2				26	17.2	α
" (3)	4				24	16.5	β
" (4)		4			28	17.9	α
" (5)			4		23	15.2	β
" (6)				4	25	15.4	β
" (7)	2		2		23	15.8	β
Comp. Ex. (1)	(Cross-linking monomer was not used)				53	19.3	β
" (2)	6				19	10.4	γ

BDMA: Butylene glycol dimethacrylate.

EXAMPLE 6

(1) Preparation of cross-linked polymer (B):

The following compounds were charged in the same reaction vessel as in Example 1-(1) and the procedure of Example 1-(1) was repeated to obtain cross-linked polymer (B) in the form of beads.

5	Styrene	60 parts	5
	n-Butyl acrylate	20	
	Methyl methacrylate	20	
	Allyl methacrylate	3.0	
	t-Dodecylmercaptan	0.1	
10	Lauroyl peroxide	0.5	10
	Polyvinyl alcohol	1.0	
	Water	200	

The resulting beads had the following particle size distribution and an average particle diameter of 77 μ .

15	Mesh	wt. %	15
	Lower than 32	3.4	
	32 — 48	13.3	
	48 — 100	57.1	
	100 — 150	15.1	
20	150 — 200	7.6	20
	200 — 250	3.1	
	250 — 400	0.3	
	Higher than 400	0.1	

(2) Variation in effects of delustering agent on rigid PVC depending on particle sizes:

25 Cross-linked polymer (B) was sieved to divide the same into groups shown in Table 6-(1).
Compositions were prepared in the same manner as in Example 1-(2) except that the respective fractions of polymer (B) were used. 60° Specular glosses of them were measured in the same manner as above to obtain the results shown in Table 6-(1). 25

TABLE 6 - (1)

Particle size	Average particle diameter (μ)	60° Gloss
Lower than 32 mesh (Larger than 500 μ)	600	64
32 - 48 mesh (297 - 500 μ)	345	43
48 - 100 mesh (149 - 297 μ)	196	31
100 - 150 mesh (105 - 149 μ)	123	25
150 - 250 mesh (63 - 105 μ)	82	22
250 - 400 mesh (37 - 63 μ)	48	28
Higher than 400 mesh (Smaller than 37 μ)	17	55

It is apparent from Table 6-(1) that the delustering effects of the cross-linked polymer having a particle diameter of larger than 500 μ or smaller than 35 μ are very poor.

(3) Variation in effects of delustering agent on ABS resin depending on particle sizes:

Compositions were prepared in the same manner as in Example 3 except that fractions of cross-linked polymer (B) sieved in the same manner as above step (2) were used. 60° Specular glosses and Izod impact strengths of the compositions were measured to obtain the results shown in Table 6-(2).

TABLE 6 - (2)

Particle size	Average particle diameter (μ)	60° Gloss	Izod impact strength (kg.cm/cm ²)
Lower than 32 mesh (Larger than 500 μ)	600	44	14.7
32 - 48 mesh (297 - 500 μ)	345	36	20.3
48 - 100 mesh (149 - 297 μ)	196	34	22.9
100 - 150 mesh (105 - 149 μ)	123	33	23.6
150 - 250 mesh (63 - 105 μ)	82	37	23.5
250 - 400 mesh (37 - 63 μ)	48	42	23.1
Higher than 400 mesh (Smaller than 37 μ)	17	74	24.2

It is apparent from Table 6-(2) that the influences of the particle size of the cross-linked polymer

on ABS resin are significant and that the preferred results are not obtained when the particles are larger than $500\ \mu$ or smaller than $35\ \mu$.

EXAMPLE 7

100 Parts of a resin of film-forming methyl methacrylate polymer (a product of Mitsubishi Rayon Co.) were mixed with 8 parts of cross-linked polymer (B) obtained in Example 6. The composition was extruded through an extruder having a screw of a diameter of 40 mm at 230°C and cut into pellets. The resulting pellets were dried and shaped into a film of a thickness of about $50\ \mu$ by T-die method by means of the same extruder as above at 230°C . 60° Specular gloss and physical property (Tear strength) of the film were evaluated to obtain the results shown in Table 7. For comparison, pellets were prepared in the same manner as above except that cross-linked polymer (B) was not used and then the pellets were shaped into a film, the properties of which were also examined to obtain the results shown in Table 7.

TABLE 7

	60° Gloss	Tear strength (Kg/cm)
Example 7	21	1.79
Comparative Example (free of delustering agent)	88	1.75

It is apparent from Table 7 that when the cross-linked polymer of the present invention was incorporated in the film-forming methyl methacrylate polymer resin, an excellent delustering effect was exhibited without substantially deteriorating the film-forming properties thereof or physical properties of the resulting film.

EXAMPLE 8

The following compounds were charged in the same reaction vessel as in Example 1-(1) and the procedure of Example 1-(1) was repeated to obtain cross-linked polymer (C) in the form of beads.

	Methyl methacrylate	45 parts	
	n-Butyl methacrylate	45	
	Styrene	10	
	Allyl methacrylate	2	
25	n-Octylmercaptan	0.1	25
	Lauroyl peroxide	1	
	Polyvinyl alcohol	1	
	Water	200	

The resulting beads had an average particle diameter of about $60\ \mu$ according to a microphotograph. 7 Parts of cross-linked polymer (C) were incorporated in 100 parts of a methacrylic resin (ACRYPET® MDK; a product of Mitsubishi Rayon Co.) and the whole was mixed thoroughly. The mixture was extruded through an extruder having a screw of a diameter of 40 mm at 210°C and cut into pellets. The resulting pellets were dried and extrusion-molded into a plate of a thickness of 3 mm by means of the same extruder as above and 60° Specular gloss thereof was measured.

From the same pellets as above, a plate of a thickness of 3 mm was also obtained by injection molding technique at 220°C and 60° Specular gloss thereof was also measured. The results of the measurement are shown in Table 8, wherein results obtained when no delustering agent was used and when only fractions of the same cross-linked polymer which passed a sieve of 500 mesh ($25\ \mu$) were used are also shown.

TABLE 8

	60° Gl ss	
	Extrusion-molded plate	Injection-molded plate
Example 8	22	36
Comparative Example (1) (free of delustering agent)	135	140
Comparative Example (2) (containing fractions of cross-linked polymer (C) which passed a 500 mesh sieve; average particle diameter 12 μ)	49	81

It is apparent from Table 8 that the cross-linked polymer used in the present invention exhibits an excellent delustering effect also on methacrylic resin but its delustering effect is remarkably reduced when average particle diameter thereof is smaller than 35 μ .

5 EXAMPLE 9

The following compounds were charged in the same reaction vessel as in Example 1-(1) and the procedure of Example 1-(1) was repeated to obtain cross-linked polymers.

5

	Methyl methacrylate	70 parts	
	n-Butyl acrylate	30	
10	Cross-linking monomer	Amount (parts shown in Table 9	10
	Benzoyl peroxide	0.5	
	Calcium tertiary phosphate	1.0	
	Surfactant	0.01	
15	Water	200	15

The resulting polymers had an average particle diameter of about 100 μ in all cases.

Plates of a thickness of 3 mm were extrusion-molded in the same manner as in Example 8 except that the above cross-linked polymers were used. 60° Specular glosses of them were measured to obtain the results shown in Table 9.

TABLE 9

	Cross-linking monomer				Physical properties	
	Allyl methacrylate	Triallyl cyanurate	EDMA	Divinyl- benzene	60° Gloss	Surface conditions
Experiment (1)	1				42	α
" (2)	2				27	α
" (3)	4				21	β
" (4)		4			29	α
" (5)			4		32	β
" (6)				4	34	β
" (7)	2		2		26	β
Comparative Experiment (1)	Cross-linking monomer was not used				103	α
" (2)	6				16	γ

EDMA: Ethylene glycol dimethacrylate

EXAMPLE 10

The following compounds were charged in the same reaction vessel as in Example 1-(1) and the procedure of Example 1-(1) was repeated to obtain a cross-linked polymer.

	Methyl methacrylate	25 parts	
5	n-Butyl acrylate	30	5
	Styrene	45	
	Allyl methacrylate	2	
	t-Dodecylmercaptan	0.2	
	Lauroyl peroxide	1.0	
10	Polyvinyl alcohol	1.0	10
	Water	200	

The resulting polymer had an average particle diameter of about 60 μ .

100 Parts of a resin of film-forming methyl methacrylate polymer (a product of Mitsubishi Rayon Co.) were mixed thoroughly with 8 parts of the cross-linked polymer. The mixture was extruded through an extruder having a screw of a diameter of 40 mm at 230°C and cut into pellets. The resulting pellets were dried and extruded by means of the same extruder at 230°C to obtain a film having a thickness of about 50 μ . 60° Specular gloss and a physical property (Tear strength) were examined. The results are shown in Table 10, wherein the results obtained when the cross-linked polymer was not added are also shown.

TABLE 10

	60° Gloss	Tear strength (Kg/cm)
Example 10	23	1.69
Comparative Example (free of delustering agent)	88	1.75

It is apparent from Table 10 that when the cross-linked polymer used in the present invention is incorporated in the film-forming methyl methacrylate polymer resin, an excellent delustering effect can be exhibited without substantially deteriorating physical properties or the film-forming property.

EXAMPLE 11

25 The following compounds were charged in the same reaction vessel as in Example 1-(1) and the same procedure as in Example 1-(1) was repeated to obtain a cross-linked polymer. 25

	Methyl methacrylate	60 parts	
	Styrene	20	
	Acrylonitrile	20	
30	Triallyl cyanurate	3	30
	n-Octylmercaptan	0.1	
	Azobisisobutyronitril	0.2	
	Polyvinyl alcohol	1.0	
	Water	200	

The resulting polymer had an average particle diameter of about 70 μ .
 100 Parts of ABS resin (DIAPET 3001; a product of Mitsubishi Rayon Co.) were mixed thoroughly with 5 parts of the cross-linked polymer by means of a Henschel mixer. The mixture was extruded through an extruder having a screw of a diameter of 40 mm at 230°C and cut into pellets.
 5 The resulting pellets were dried and then injection-molded into a plate of a thickness of 3 mm at 200°C. 60° Specular gloss and Izod impact strength of the plate were measured. The results are shown in Table 11, wherein the results obtained when the cross-linked polymer was not used are also shown.

TABLE 11

	60° Gloss	Izod impact strength, (kg.cm/cm ²)
Example 11	38	21.6
Comparative Example (free of delustering agent)	95	25.1

10 It is apparent from Table 11 that the cross-linked polymer used in the present invention exhibits an excellent delustering effect on ABS resin and causes only a relatively small reduction in physical properties.

EXAMPLE 12

100 Parts of polyvinyl chloride (\bar{P} =720) were mixed thoroughly with 3 parts of a stabilizer (dibutyltin maleate), 10 parts of a high impact resistance aid (METABLEN © C—102; a product of Mitsubishi Rayon Co.), 1 part of a lubricant (butyl stearate), 1 part of a processing aid (METABLEN © P—551; a product of Mitsubishi Rayon Co.) and 5 parts of cross-linked polymer (C) obtained in Example 8. The mixture was kneaded by means of rolls at 160°C and 60° Specular gloss of the resulting sample was measured. Then, the sample obtained by the kneading with rolls was compression-molded into a plate of a thickness of 2.5 mm at 165°C under 70 tons and V-notch Izod impact strength thereof was measured.

The results of the measurement were shown in Table 12, in which the results obtained when cross-linked polymer (C) was not used are also shown.

TABLE 12

	60° Gloss	Izod impact strength, (kg.cm/cm ²)
Example 12	24	15.7
Comparative Example (free of delustering agent)	85	21.2

25 It is apparent from Table 12 that the cross-linked polymer used in the present invention exhibits an excellent delustering effect on polyvinyl chloride resin without substantially causing reduction in physical properties such as impact resistance.

EXAMPLE 13

As comparative example, following compounds were charged in the same reaction vessel as in
 30 Exmpl 1-(1):

Styren	70 parts
Ethyl acrylate	30
Allyl methacrylat	2.5

n-Octylmercaptan	0.1 part
Potassium persulfat	0.3
Emulsifier	2.0 parts

After sufficiently replacing the gas in the reaction vessel with nitrogen gas, the mixture of the above compounds was heated to 70°C under stirring and kept at that temperature for 5 hours to complete the emulsion polymerization.

The particles in the resulting latex had a diameter of 0.2—0.4 μ according to photo-extinction method. 5 Parts of calcium chloride were added to the latex to effect the salting-out. After dehydration, washing with water and drying, a cross-linked polymer in the form of a powder was obtained. A composition was obtained in the same manner as in Example 1-(2) except that the powdery cross-linked polymer obtained by the above method was used, or no said polymer was used. 60° Specular gloss of the product was examined. The results are shown in Table 13.

TABLE 13

	Amount of the powdery cross-linked polymer	60° Gloss
Experiment 1	5 parts	78
" 2	25 parts	72
" 3	None	83

It is apparent from Table 13 that the particles of small diameters as obtained by the emulsion polymerization have substantially no delustering effect.

CLAIMS

1. A delustered thermoplastic resin composition which comprises a thermoplastic resin and a cross-linked polymer having an average particle diameter of 35—500 μ obtained by suspension-polymerizing a non-cross-linking monomer composition comprising 0—90 wt.% of a vinyl aromatic monomer, 10—100 wt.% of a monomer which is an alkyl acrylate or alkyl methacrylate having 1-13 carbon atoms in the alkyl group and 0—40 wt.% of another monoethylenically unsaturated monomer with 0.5—5 parts by weight, per 100 parts by weight of the non-cross-linking monomer composition, of a cross-linking monomer having at least two double bonds in the molecule.

2. A delustered thermoplastic resin composition according to Claim 1 wherein the non-cross-linking monomer composition comprises 40—100 wt.% of the alkyl acrylate or alkyl methacrylate.

3. A delustered thermoplastic resin composition according to Claim 1 or Claim 2 which comprises not more than 40 parts by weight of the cross-linked polymer per 100 parts by weight of the thermoplastic resin.

4. A delustered thermoplastic resin composition according to any preceding Claim wherein the cross-linking monomer is a compound containing at least one allyl group.

5. A delustered thermoplastic resin composition according to any preceding Claim wherein average particle diameter of the cross-linked polymer is 40—200 μ .

6. A delustered thermoplastic resin composition according to any preceding Claim wherein the thermoplastic resin is selected from polyvinyl chloride, ABS resin, methacrylic resin, acrylic resin, methyl methacrylate-butadiene-styrene resin, nylon resin, polyethylene resin, polyethylene terephthalate resin, polybutylene terephthalate resin, polycarbonate resin, polyurethane resin, polystyrene resin, high impact resistance styrene resin and polypropylene resin.

7. A delustered thermoplastic resin composition according to Claim 1, substantially as herein described with reference to any of the Examples.

8. A process for producing a delustered thermoplastic resin composition which comprises incorporating in a thermoplastic resin a cross-linked polymer having an average particle diameter of 35—500 μ which polymer is obtained by suspension-polymerizing a non-cross-linking monomer composition comprising 50—90 wt.% of a vinyl aromatic monomer, 10—50 wt.% of a monomer which is an alkyl acrylate or alkyl methacrylate having 1—13 carbon atoms in the alkyl group and 0—40 wt.% of another monoethylenically unsaturated monomer with 0.5—5 parts by weight, per 100 parts by weight of the non-cross-linking monomer composition, of an allyl compound having at least two double bonds in the molecule and, if necessary, up to 5 parts by weight of another cross-linking monomer.

9. A process according to Claim 8 substantially as herein described with reference to any of the Examples.

10. A delustered thermoplastic resin composition made by a process according to Claim 8 or Claim 9.

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